THE ELECTROLYSIS OF SALTS OF ALKYLOXYACIDS.

by

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C O N T E N T S .

INTRODUCTION.

In 1849 Kolbe [1] identified ethane amongst the products of electrolysis of a concentrated solution of potassium acetate. Its formation was regarded as being due to the interaction of two discharged anions according to the following scheme:-

$$CH_3COOK \longrightarrow \dot{K} + CH_3COO.$$

$$2CH_3COO \longrightarrow 2CO_2 + CH_3\text{-}CH_3.$$

Forty years later Crum Brown & Walker applied this synthetic method to the series of dibasic acids. They electrolysed concentrated aqueous solutions of the potassium ethyl salts of these acids and obtained the di-esters of the higher members of the series:- [2]

$$2\ \begin{matrix}COOEt\\|\\(CH_2)_n\\|\\COOK\end{matrix} \longrightarrow 2K + 2CO_2 + \begin{matrix}COOEt\\|\\(CH_2)_{2n}\\|\\COOEt\end{matrix}$$

The potassium ethyl salts of the alkyl-substituted malonic acids also gave the synthetic product, although in smaller yield than was the case with malonic acid itself, owing to the formation of larger quantities of unsaturated compounds as by-products.

Many attempts have since been made to extend this synthesis to substituted acids of various kinds. In general, however, it has been found that the

(1) Ann., 69, 257.
(2) Trans. Roy. Soc. Edinburgh, 36, 211; Ann., 261, 107.

introduction of substituent groups into the molecule prevents the normal synthesis from taking place.

PREVIOUS INVESTIGATIONS ON THE ELECTROLYSIS OF SALTS OF HYDROXY- AND ALKYLOXYACIDS.

From the first, attempts to apply the Kolbe synthesis to hydroxyacids have resulted in failure. Except in the case of mandelic acid, from which a little hydrobenzoin can be obtained, no instance of direct synthesis has ever been recorded. Miller & Hofer [1] and J.W.Walker [2] electrolysed sodium glycollate, and found that formaldehyde was the chief organic product. Potassium lactate gave acetaldehyde, and sodium α-hydroxybutyrate gave propionic aldehyde. Neuberg [3] electrolysed a salt of d-gluconic acid in the hope of synthesising a polyhydric alcohol of ten carbon atoms. He obtained, however, d-arabinose; other polyhydroxyacids behaved in a similar manner.

The expedient of protecting the hydroxyl group by substituting for its hydrogen atom an alkyl group naturally suggested itself. Miller & Hofer [1] electrolysed salts of methoxyacetic acid. They

(1) Ber., 27, 461.
(2) Jour. Chem. Soc., 69, 1278.
(3) Biochem. Zeitschr., 7, 527.

found that, as with glycollic acid, the chief product was formaldehyde; formic acid, methylal, and methyl alcohol appeared in small quantity. J.W.Walker obtained likewise no synthetic product, or indeed any oily layer at all, by electrolysing sodium ethoxyacetate.

Crum Brown & Bolam [1] state that in the cases of methoxyacetic and ethoxysuccinic acids, the anion is completely broken up. With the potassium ethyl salt of unsymmetrical diethoxysuccinic acid, however, they obtained an oily layer which they believed to be the synthetic product, the di-acetal of diketoadipic ester.

The only successful synthesis of this kind was carried out by Hamonet [2] in 1905. In attempting to find a method of preparation of tetramethylene glycol, he electrolysed sodium β-amyloxypropionate, and obtained in good yield the diamyl ether

$$(C_5H_{11}O)CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2(O\cdot C_5H_{11}).$$

He used the amyl derivative as much to avoid fiscal restrictions on the use of ethyl alcohol as to increase the molecular weight of the acid electrolysed. He also investigated the behaviour of salts of other similar acids when subjected to electrolysis, such as amyloxyacetic, α-amyloxypropionic, γ-amyloxybutyric. He found that when the

(1) Proc. Roy. Soc. Edinburgh, 22, 255.
(2) Bull. Soc. Chim., 33, 513.

alkyloxy- group was in the α- or γ- position, "inextricably complex mixtures of an acetallic nature" were produced, and no synthesis took place.(1) This behaviour he attributed to the ease of hydrolysis of the acid according to the equation:-

$$R\text{-}CH(OC_5H_{11})COOH + H_2O \longrightarrow R\text{-}CH(OH)COOH + C_5H_{11}OH.$$

The current then acting on the hydroxyacid, formed acetallic products.

Miller & Hofer accounted for the formation of formaldehyde when salts of glycollic acid are electrolysed, by assuming that after the discharged anion has lost carbon dioxide, it is oxidised:-

$$CH_2(OH)COO \longrightarrow CH_2(OH) \longrightarrow CH_2O.$$

Hofer & Moest (2) later obtained alcohols by electrolysis of salts of fatty acids in presence of substances which yielded hydroxyl ions at the anode (e.g. perchlorates, bicarbonates etc.) , and advanced the theory that the discharged anion interacted with hydroxyl according to the equation

$$RCOO + OH \longrightarrow ROH + CO_2.$$

They suggested that glycollic acid would yield formaldehyde if a similar reaction took place:-

$$CH_2(OH)COO + OH \longrightarrow CH_2\begin{matrix}OH\\OH\end{matrix} + CO_2.$$

The intermediate compound, being incapable of

(1) Comptes Rendues, 132, 259;
Bull. Soc. Chim., 33, 534.
(2) Ann., 323, 322.

existence, appears as formaldehyde and water:-

$$CH_2(OH)_2 \longrightarrow CH_2O + H_2O.$$

It is clear, however, that the same end products would result in whatever way the intermediate compound had been formed, and we are led to enquire as to what other modes of formation of the alcohol ROH by electrolysis of the salt RCOOK have been suggested.

The alcohol may result through the formation and subsequent hydrolysis of the ester RCOOR:-

$$2RCOO \longrightarrow CO_2 + RCOOR.$$

$$RCOOR + H_2O \longrightarrow ROH + RCOOH.$$

Kolbe observed the production of methyl acetate from potassium acetate,(1) and butyl valerate from potassium valerate.(2) Bouveault found that on electrolysing potassium ethyl succinate, a twentieth part of the product consisted of ethyl hydracrylate. He attributed its formation to a reaction between two discharged anions and one water molecule:-

$$2RCOO + H_2O \longrightarrow ROH + RH + 2CO_2.$$

and he identified, moreover, in the electrolytic product the ethyl propionate (RH) demanded by the equation.(3)

Hamonet (4) has stated that alcohols are

(1) Ann., 69, 285.
(2) ibid., 267.
(3) Bull. Soc. Chim., 29, 1044.
(4) Comptes Rendues, 123, 252.

always formed to the extent of a third or more of the product, but that they are apt to be overlooked, being usually soluble in the aqueous layer. He suggested as a possible means of their formation the hydration of unsaturated compounds produced according to Crum Brown & Walker's equation:-

$$2C_nH_{2n+1}COO \longrightarrow CO_2 + C_nH_{2n} + C_nH_{2n+1}COOH.$$

OBJECT OF THE PRESENT WORK.

This research was undertaken in order to investigate somewhat more closely the behaviour of salts of alkyloxyacids on electrolysis. In particular it was thought that it might be possible to ascend the series of dibasic hydroxyacids (i.e. tartronic, tartaric, mucic etc.) by electrolysis of the potassium ethyl salts of their alkyl derivatives, in an analogous manner to Crum Brown & Walker's synthesis of the normal dibasic acids.

Accordingly the potassium ethyl salts of ethoxymalonic and symmetrical d-diethoxysuccinic acids have been prepared, and their aqueous solutions electrolysed.

In addition, the electrolysis of potassium ethoxyacetate has been repeated in order to see whether its behaviour was in reality different from that of the methoxyacetates; and sodium amyloxyacetate has also been electrolysed with the object of ascertaining the effect of the amyl group on the composition of the resulting product.

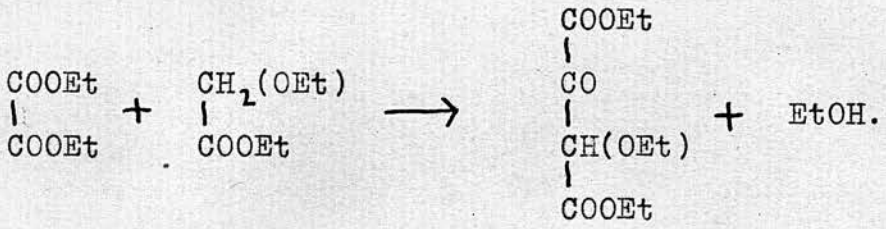
In the course of the investigation several new compounds have been prepared, and the dissociation constants of ethoxymalonic acid and d-diethoxysuccinic acid have been determined.

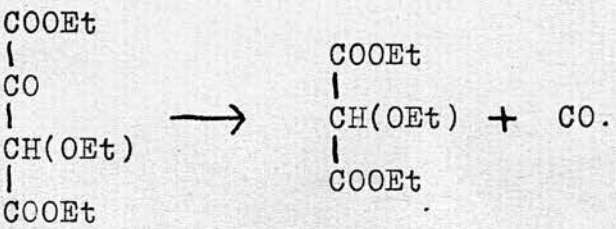
EXPERIMENTAL.

PREPARATION OF ETHYL ETHOXYMALONATE.

This compound cannot be prepared by the action of sodium ethoxide on ethyl chloromalonate, since the remaining hydrogen atom of the chloroester is replaceable by sodium, and condensation takes place with formation of tetracarboxylic esters.(1)

Recourse was therefore had to the method of Wislicenus & Münzesheimer,(2) who prepared it from ethyl ethoxyoxalacetate. This can readily be obtained by condensing ethyl oxalate with ethyl ethoxyacetate in presence of sodium ethoxide. When the oxalester is heated, it breaks down into ethyl ethoxymalonate and carbon monoxide.





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(1) Conrad & Guthzeit, Ann. 214, 76.
Bischoff, Ber. 29, 1288.

(2) Ber. 31, 552.

ETHYL ETHOXYACETATE.[1] 50 gms. of ethyl chloracetate were added in small portions at a time to a solution of sodium ethoxide made by dissolving 9·5 gms. of sodium (slightly more than one atomic proportion) in 180 c.c. of absolute alcohol. The temperature was maintained between 40 and 50° by the heat of the reaction, any tendency to rise above 50° being checked by cooling the flask in water. A copious precipitate of salt appeared, and the mixture was allowed to stand overnight.

In order to decompose any remaining sodium ethoxide, carbon dioxide was passed into the mixture, which was then filtered. The filtrate when distilled yielded 37 gms. of nearly pure ester, i.e. 68 per cent. of theory.

The crude ester was freed from alcohol by repeated fractionation, and was obtained as a colourless liquid of b.p. 154-155°.

Similar preparations under different temperature conditions gave poor yields. In the cold (i.e. by cooling under the tap while adding the chloroester) a yield of 13 per cent. was obtained. On the other hand a high temperature during the reaction followed by half an hour on the water bath, gave a 14 per cent. yield with slight discolouration.

(1) Henry, Ber. 4, 706; Schreiner, Ann. 197, 8.

ETHYL ETHOXYOXALACETATE.[1] Instead of preparing dry sodium ethoxide and dissolving it in an ethereal solution of ethyl oxalate, as described by Wislicenus & Scheidt, metallic sodium was treated under ether with the calculated quantity of alcohol, small additions of ethyl oxalate being made from time to time in order to dissolve the solid ethoxide. The ether-soluble additive compound $EtOOC.C(ONa)(OEt)_2$ was presumably formed. In this way the inconvenience of preparing dry sodium ethoxide was avoided.

18 gms. of sodium in thin slices was covered with 340 c.c. of dry ether, and 36 gms. of absolute alcohol run in from a burette. When the action had come to an end owing to the sodium becoming covered with ethoxide, small portions of ethyl oxalate were added. The ethoxide was thereby dissolved with evolution of heat (which, however, was no longer evident after one molecular quantity of the ester had been added) exposing afresh the surface of the sodium. In all, 140 gms. of ethyl oxalate were added. This represents an excess of 26 gms. With the cold clear solution obtained in this way, 102 gms. of ethyl ethoxyacetate was mixed, and the whole allowed to stand for several days.

Rather more than an equal bulk of water was now added, and the ethereal layer, containing the

(1) Wislicenus & Scheidt, Ber. 24, 432.

excess of ethyl oxalate, separated off. The aqueous layer, containing the sodium compound of the oxalester, was treated with the calculated quantity of dilute sulphuric acid, saturated with salt, and extracted several times with ether. The ether was removed, and the residual pale yellow oil distilled under reduced pressure. After a little water had come over, the temperature rose rapidly, and the bulk of the product passed over at 125-130° at 7·5 mm.

Yield 136 gms. = 75 per cent. of theory.

The ester is slightly soluble in water, and is a viscous, colourless and almost odourless oil of sp. gr. 1·128 at 15/15°.

DECOMPOSITION OF ETHYL ETHOXYOXALACETATE.

The ethyl ethoxyoxalacetate was heated in a stream of carbon dioxide at a temperature of 180°, slowly rising to 200° in the course of one or two hours. Carbon monoxide was evolved freely and could be made to burn, even when diluted with the carbon dioxide, at the end of the condenser. The progress of the decomposition was followed by the ferric chloride reaction given by the oxalester in alcoholic solution. The reaction was also seen to be at an end when no further evolution of gas occured. The

temperature was then raised, and the crude ethyl ethoxymalonate distilled over.

This was fractionated, and obtained as a colourless oil of b.p. 226-229·5°. (Wislicenus & Münzesheimer give 228°).

Yield from 337 gms. of ethyl ethoxyoxalacetate, 226 gms. or 75 per cent. of theory.

POTASSIUM ETHYL ETHOXYMALONATE.

20 gms. of the ester was dissolved in half a litre of rectified spirits, and the calculated quantity of alcoholic potash for half saponification added. The mixture was neutral to phenolphthalein (on addition of water to a test portion) in a few hours, and a small precipitate appeared. This was the dipotassium salt which is insoluble in alcohol. It was filtered off, and the alcohol removed by distillation on the water-bath at 100 mm. pressure. The viscous mass remaining was dissolved in 20 c.c. of water, extracted twice with ether to remove unchanged ester, and electrolysed at once.

On standing in aqueous solution in the cold, or more rapidly on warming, the potassium ethyl salt decomposes, with formation of an oil having the

odour of ethyl ethoxyacetate.

The dry substance can be obtained by allowing the aqueous solution to stand in a vacuum desiccator over sulphuric acid. It is a white, glassy mass, very deliquescent and miscible with alcohol and water.

ELECTROLYSIS OF POTASSIUM ETHYL ETHOXYMALONATE.

This operation was carried out in a platinum crucible which functioned as cathode. The anode consisted of a spiral of platinum wire 26 mm. in diameter coiled so as nearly to touch the crucible. It was prevented from actually doing so by thin glass rods suspended from the edge of the crucible. In this way the internal resistance was reduced to a minimum. The crucible was cooled during electrolysis by immersion in running water, the temperature of the contents being kept below 25°.

A current of 3 amperes at 10 volts was passed for an hour, when the oil formed was separated off. The residual liquid was again electrolysed for an hour. The whole was then extracted with ether. The ethereal extract was dried over calcium chloride, and contained about 4 gms. of oil in each case, i.e.

from 20 gms. of di-ester. Total amount of oil obtained in this way, 36 gms.

Area of anode surface = 4·36 sq. cms.

Current density = 69 amperes per sq. dec.

INVESTIGATION OF THE PRODUCTS OF ELECTROLYSIS.

Aqueous residue. During the last stages of the electrolysis potassium bicarbonate crystallised out from the liquid. It was also found to contain ethyl alcohol, oxalic acid, formaldehyde, and acetaldehyde.

Oily product. The oil was distilled under reduced pressure. The lower boiling portions were refractionated under ordinary pressure, and the higher boiling portion under reduced pressure. Four main fractions were in all obtained:-

1. 75-80°.
2. 130-145°.
3. 190-200°.
4. 150-165° at 15 mm.

1. This was small in quantity and was identified as ethyl alcohol.
2. When freshly distilled this fraction had an odour somewhat resembling that of formaldehyde. It had strong reducing properties, giving a silver mirror readily with ammoniacal silver hydroxide,

and reducing Fehling's solution on gentle warming. It coloured Schiff's reagent.

When oxidised with dilute nitric acid, oxalic acid was produced.

After purification by further distillations, it was obtained boiling between 137 and 140°.

The alcoholate of ethyl glyoxylate has a b.p. of 136-138°.

With aniline acetate and acetic acid, a white crystalline precipitate which turned bright yellow on standing was obtained. This reaction is characteristic of glyoxylic acid.

·1502 gm. of the liquid gave ·2666 gm. carbon dioxide and ·1049 gm. water.

Found C = 48·40, H = 7·83. $C_6H_{12}O_4$ requires C = 48·64, H = 8·11 per cent.

The phenylhydrazone was prepared and recrystallised twice, from alcohol and water, and from chloroform and ligroin. Its m.p. was found to be 128-129° (uncorr.). The phenylhydrazone of ethyl glyoxylate has a m.p. of 131°.

·1095 gm. gave 12·89 c.c. of nitrogen at N.T.P.

Found N = 14·72. $C_{10}H_{12}O_2N_2$ requires N = 14·58 per cent.

3. This fraction was the main product of the electrolysis, being the largest of the four. It had a slight fruity odour.

A molecular weight determination by the Beckmann boiling point method gave a value of 180. The solvent used was benzene.

When warmed with dilute hydrochloric acid, alcohol was liberated and an oily substance left which gave all the reactions of glyoxylic ester. The original substance gave no reactions characteristic of aldehydes.

By evaporating on the steambath with concentrated hydrochloric acid, glyoxylic acid was obtained. The phenylhydrazone when recrystallized from water, appeared as short yellow needles of m.p. 136-137°, thus establishing the identity of the acid. When preparing this compound it was found that the presence of hydrochloric acid was essential.(1)

The molecular weight of ethyl diethoxyacetate is 176, and its b.p. is 199°. The substance under investigation was identified with this by conversion into diethoxyacetamide. It was treated with concentrated ammonia and sufficient alcohol to keep it in solution, and allowed to stand overnight. A crystalline mass was left after evaporation in the cold over sulphuric acid, which was taken up in ether, filtered and again evaporated. The amide was recrystallised twice

(1) cf. Elbers, Ann. 227, 353

from chloroform and petroleum ether. Its m.p. was 79-80°.

This solvent gave two distinct crystalline forms in different operations:- (1) The characteristic thin transparent plates, flexible and greasy to the touch [1]; and (2) long needles. The melting points of the two forms were identical. The substance is known to sublime in needles.

4. This fraction was small in quantity. In order to detect the presence of any ethyl diethoxy-succinate, which, if any synthesis had taken place, would be expected here, 2 gms. were heated with 20 gms. of hydrφiodic acid (sp. gr. 1·82) in a sealed tube to 100° for eight hours. The resulting mixture was distilled under reduced pressure to remove the ethyl iodide and most of the hydrφiodic acid. The remainder was taken off in a vacuum desiccator over caustic soda. The sticky residue was dissolved in water and filtered from iodine. The filtrate was extracted repeatedly with petroleum ether until the remaining iodine was removed. It was then evaporated on the steambath.

The following reactions indicated the presence of tartaric acid:-

The syrupy residue, when heated, charred and

(1) Schreiber, Jahrsb. der Chem., 1870, 642.

gave an odour of burnt sugar.

It gave the colour reactions when warmed with concentrated sulphuric acid and resorcinol (red), and pyrogallol (purple).

A neutral solution gave with calcium chloride solution a precipitate soluble in acetic acid on warming; and with silver nitrate a precipitate which gave a metallic mirror when dissolved in dilute ammonia and warmed.

A solution of the substance prevented precipitation of copper hydroxide by sodium hydroxide.

A white crystalline precipitate was obtained with potassium acetate and alcohol. This was recrystallised from water, and when seen under the microscope, appeared to be identical with crystals of potassium hydrogen tartrate. The quantity was too small to admit of quantitative estimation.

ETHOXYMALONAMIDE.

Ethyl ethoxymalonate was treated with excess of concentrated ammonia and sufficient alcohol to keep it in solution. The amide was obtained on evaporation and was recrystallised twice from rectified spirits. Its m.p. was found to be 203-204°.

·00846 gm. combusted in a micronitrogen apparatus [1] gave 1·420 c.c. of nitrogen at 21° and 766·6 mm.

Found N = 19·26; $C_5H_{10}O_3N_2$ requires N = 19·17 per cent.

ETHOXYMALONIC ACID.

The free acid was found to be very soluble in water, and to decompose somewhat at 100°. The following method was therefore adopted for isolating it. Potassium ethoxymalonate was treated with excess of hydrochloric acid and the solution taken to dryness at 50° in a vacuum. The residue was extracted with ether. The acid crystallised on removal of the ether.

It was recrystallised from a mixture of ethyl acetate and petroleum ether. Melting point 124-126°

(1) Pregl: Die Quant. Org. Mikroanalyse (1923), 86.

with decomposition.

·0952 gm. of the acid required 25·66 c.c. of N/20 alkali for neutralisation. The calculated figure is 25·70 c.c.

Dissociation Constant. A solution of the acid was adjusted to an exact concentration of 1/16 molecular normal by titration with baryta, and the conductivity taken. The subsequent dilution was performed according to Arrhenius' method, and readings up to a dilution of 2048 litres were obtained.

The values for the conductivity and dissociation constant are shown in the table below, in which

v = vol. in litres containing 1 gm. mol.,

μ = conductivity in mhos. at 25°,

μ_∞ = conductivity at infinite dilution,

m = degree of dissociation = $\frac{\mu}{\mu_\infty}$,

and K is the constant calculated from the formula

$$K = 100 \frac{m^2}{(1-m)v} .$$

Temp. = 25°.

V.	μ	100m.	K.
16	105·9	28·54	·71
32	138·9	37·44	·70
64	176·8	47·65	·68
128	218·2	58·82	·66
256	262·5	70·75	·67
512	300·1	80·87	·67

$\mu_\infty = 371.$ $K = \cdot 71.$

The value of 371 for μ_∞ is that given by Ostwald [1] for an acid having 18 atoms in the molecule.

Conductivity of water used = 1×10^{-6} mhos.

Weak dibasic acids behave at moderate dilutions as monobasic acids in as far as they dissociate into one hydrogen ion and the residue of the molecule. But as this dissociation approaches completion, the secondary reaction

$$R\begin{matrix}\diagup COO' \\ \diagdown COOH\end{matrix} = R\begin{matrix}\diagup COO' \\ \diagdown COO'\end{matrix} + H^{\cdot}.$$

commences, and Ostwald's dilution law no longer holds with accuracy.

In the case of a comparatively strong acid such as ethoxymalonic, the disturbing factor at high dilutions would be expected to be great. The "constant" was found, in fact, to be five times as great at a dilution of 2048 litres as at 512 litres.

TARTRONIC ACID.

In order to compare the constants of ethoxymalonic and tartronic acids, a specimen of the

(1) Ostwald-Luther: Phys. Chem. Messungen 3rd. ed. p. 482.

latter acid was prepared. Two values have been given for K, namely ·107 by Ostwald,[1] and ·5 by Skinner.[2] The second of these, as Skinner points out, is of the order that would be expected, since malonic acid shows a value of ·158, and the introduction of a hydroxyl group should increase the strength of the acid.

The value obtained for ethoxymalonic acid indicated that Ostwald's value was much too low, and this was confirmed by another determination of the constant for tartronic acid.

The tartronic acid was prepared from ethyl trichlorlactate.[3] The barium salt was decomposed with dilute sulphuric acid, and a little barium chloride added to remove any excess. The solution, after concentration by distillation under reduced pressure, was evaporated to complete dryness in a vacuum desiccator over sulphuric acid. The residue was extracted in a Soxhlet apparatus with dry ether, when the acid separated out in crystalline form in the flask. This had a m.p. of 158-159°. By dissolving in ethyl acetate and precipitating with petroleum ether, the m.p. was raised to 162-163°. A recrystallisation from ether further raised it to 164-165°. No rise in m.p. took place after a third crystallisation

(1) Zeit. für Phys. Chem. 3, 369.
(2) Jour. Chem. Soc. 73, 488.
(3) Pinner, Ber. 18, 754 and 2852.

(from ethyl acetate alone), and the acid was accordingly taken as pure.

The m.p. of tartronic acid has been variously given, some figures ranging from 155 to 160°; others from 180 to 186°.

A titration with standard alkali showed that the acid was nearly, but not quite, pure. ·08178 gm. required 27·08 c.c. of N/20 alkali. The calculated figure is 27·25 c.c.

The constant obtained agrees fairly closely with that given by Skinner. The value taken for μ_∞, however, was 376 (Ostwald) as against 358.

Temp. = 25°.

V	μ_∞	100m	K
16	95·12	23·50	·54
32	125·8	33·46	·53
64	162·4	43·19	·51
128	203·7	54·17	·50
256	246·7	65·60	·49

μ_∞ = 376. K = ·54.

Conductivity of water used = 1×10^{-6} mhos.

The steady decrease in the value of the constant corresponds to that found by Skinner. It is probably due to some chemical change taking place, such as catalytic oxidation at the platinised electrodes. A similar decrease is recorded by

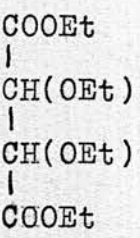
Ostwald with formic acid [1], and by Findlay, Turner, & Owen with the phenylalkyloxyacetic acids [2].

The first figure has been taken as representing the most probable value. It will be seen that the substitution of the hydroxyl group by an ethoxyl group has increased the value of the dissociation constant. A similar increase due to such a substitution has been found by Ostwald in the case of glycollic acid, and by Findlay, Turner, & Owen in the case of mandelic acid [3].

(1) Zeit. für Phys. Chem. 3, 174.
(2) Jour. Chem. Soc. 95, 938.
(3) loc. cit.

PREPARATION OF ETHYL d-DIETHOXYSUCCINATE.

In order to obtain the symmetrical compound



ethyl tartrate was ethylated by means of silver oxide and ethyl iodide. It has been shown that other methods (e.g. the action of sodium ethoxide on symmetrical ethyl dibromosuccinate) give the unsymmetrical diethoxyester.

ETHYL TARTRATE. This was prepared by the automatic method of Frankland and Aston,[1] which dispenses with the addition of a mineral acid as catalyst. The tartaric acid was esterified in batches of 150 gms. Yields of about 60 per cent. were obtained, the apparatus being kept running for ten hours. By substituting at this stage absolute alcohol and calcium carbide for the rectified spirits and potassium carbonate, the yield was increased by only 5 per cent. after a further ten hours.

The ester, obtained from the reaction mixture by distillation under reduced pressure, was redistilled,

(1) Jour. Chem. Soc., 79, 517.

and boiled steadily at 158° at 16 mm.

ETHYLATION OF ETHYL TARTRATE.[1] 65 gms. of ethyl tartrate and 407 gms. of ethyl iodide were mixed in a litre flask, and 300 gms. of dry silver oxide added. After a short time the reaction commenced, and the temperature of the mixture rose rapidly. This was moderated by cooling the flask in water with constant shaking, and not allowed to exceed 30-40°. When the temperature showed no further signs of rising (three to four hours), the mixture was allowed to stand overnight.

It was then heated on a water-bath under a reflux for four hours to complete the reaction, when the odour of ethyl iodide gave place to that of ether. The semi-solid mass was filtered at the pump after dilution with benzene, the silver residues being washed several times with fresh benzene.

The benzene etc. was removed, and the residual oil distilled under reduced pressure. It came over within a few degrees leaving nothing in the flask. After a few distillations the ester was obtained boiling at 138-139° at 11 mm. Yield 77 gms. which represents 93 per cent. of theory.

By preventing the temperature from exceeding

(1) Purdie & Pitkeathly, Jour. Chem. Soc., 75, 159.

40°, the oxidising action of the silver oxide is almost entirely avoided, and the yield thereby increased by about 20 per cent. In preparations where the mixture was allowed to reach the boiling point of the ethyl iodide, the silver residues were quite black, and much ethyl oxalate was obtained in the final distillation. It is noteworthy that although Purdie & Pitkeathly obtained a nearly theoretical yield when using methyl iodide, this was not the case with ethyl iodide. Moreover they had difficulty in purifying the ethylated product. In a methylation, the temperature would of necessity be limited to 40-50°. The point is of importance in view of the expense of the reagents involved.

·1533 gm. of the ester gave ·3081 gm. of carbon dioxide and ·1164 gm. of water.

Found C = 54·83, H = 8·51; calculated for $C_{12}H_{22}O_6$ C = 54·92, H = 8·46 per cent.

Optical rotation of ester. The ester was placed in a 100 mm. tube and maintained at 18°.

α = +98·05°; density at 18° = 1·046.

Hence $[\alpha]_D^{18}$ = +93·74°.

Purdie & Pitkeathly give +93·23°. This figure was obtained by them after partially saponifying and then redistilling the ester to get rid of impurities which could not be removed by distillation.

POTASSIUM ETHYL DIETHOXYSUCCINATE.

The half saponification of the ester was carried out as before. Since the dipotassium salt is in this case soluble in alcohol, it was necessary to separate it from the potassium ethyl salt by other means. The separation was effected by dissolving the viscous mass, obtained on removal of the alcohol, in acetone. The dipotassium salt was filtered off and the acetone removed. The residue was then dissolved in water, extracted with ether, and the solution brought to a suitable concentration for electrolysis.

The aqueous solution, unlike that of potassium ethyl ethoxymalonate, showed no tendency to decompose on standing. The dry substance is a white brittle mass, excessively deliquescent, and miscible in all proportions with water, alcohol and acetone.

ELECTROLYSIS.

The potassium salt from 20 gms. of di-ester was dissolved in 40 c.c. of water. It was found that a more concentrated solution could not be dealt with conveniently owing to frothing taking place. The

apparatus used was the same as for the previous electrolysis.

A total of 312 gms. of di-ester was treated, yielding 80 gms. of oily electrolytic product.

INVESTIGATION OF THE PRODUCTS OF ELECTROLYSIS.

Aqueous residue. Besides potassium carbonate and bicarbonate, this contained ethyl alcohol, formaldehyde, and formic and oxalic acids.

Oily product. The oil was nearly optically inactive, indicating that in all probability little or no synthesis had taken place. It was distilled under reduced pressure and yielded two fractions boiling below 100° :-

1. Below 25° at 15 mm. (4gms.)
2. 95-103° at 12 mm. (11gms.)

The remainder was distilled at a pressure of ½ mm. using a Gaede mercury pump.

3. 80-100°. (13 gms.)
4. 125-155°. (33 gms.)

The distillation was stopped at this point as some decomposition was taking place. A residue of weight 18 gms. remained in the flask.

1. This was found to contain ethyl alcohol, formic

acid, ethyl formate and a trace of methyl alcohol.

2. Gave a blue-violet colouration with ferric chloride. It was redistilled under ordinary pressure giving:-

(a) a small quantity under 100°, identical with fraction 1.

(b) about 1 gm. between 100 and 200°, which after standing for a few months deposited some crystals of m.p. 101°. They were found to be crystals of hydrated oxalic acid; the remaining liquid was ethyl oxalate.

(c) a liquid boiling at 200-225°. It could not be further purified by distillation. A molecular weight determination in acetone gave a value of 179. Besides giving the ferric chloride reaction, it coloured Schiff's reagent, reduced Fehling's solution, gave a silver mirror with ammoniacal silver hydroxide, and reacted with phenylhydrazine. The substance was suspected to be ethyl formyl-ethoxyacetate, EtOOC.CH(OEt).CHO.

An analysis showed the following figures:-

1). ·1301 gm. gave ·2470 gm. of carbon dioxide and ·0959 gm. of water;

2). ·1743 gm. gave ·3329 gm. of carbon dioxide and ·1293 gm. of water.

Found, C = 51·79, 52·09; H = 8·26, 8·32. Calculated for $C_7H_{12}O_4$, C = 52·47, H = 7·56 per cent.

3. This fraction did not colour ferric chloride. On saponification it gave a solid acid, which proved to be oxalic acid. When treated with ammonia, oxamide was obtained. The liquid was ethyl oxalate.

The oxamide was combusted for nitrogen without further purification: ·08814 gm. gave 23·7 c.c. of nitrogen at 12·5° and 741 mm. Found, N = 31·34; calculated for $C_2H_4O_2N_2$, N = 31·81 per cent.

4. A molecular weight determination gave a value of 259. The oil was somewhat viscous, and optically inactive. It gave all the reactions shown by fraction 2(c) above with the exception of the ferric chloride reaction. It was redistilled under reduced pressure, whereby it was divided into three equal portions:- (a) below 120°, (b) 120-170°, and (c) 170-175° at 12 mm.

Each of these now coloured ferric chloride. (a) contained some ethyl oxalate. (c) was very viscous. It had a molecular weight of 262 in benzene.

In view of the fact that ethyl formyl-acetate and its derivatives are somewhat unstable compounds, and may exist in two or three isomeric modifications, it was decided at this stage to

prepare a specimen of ethyl formylethoxyacetate, which has not hithertoo been described, and examine its properties in order to facilitate its identification in the electrolytic oil.

This was accordingly done by condensing ethyl formate with ethyl ethoxyacetate in presence of sodium. For description of this preparation and the properties of the substance see later.

It was found that the behaviour of fraction 4 (wide range of boiling point and abnormal molecular weight) was similar to that of ethyl formylethoxyacetate.

With phenylhydrazine (two mols. for one of ester), a solid derivative was obtained which could easily be crystallised from chloroform, and then appeared as a canary-yellow powder. Its m.p. was 229°.

This substance was combusted in a micro-nitrogen apparatus. ·00920 gm. gave 1·484 c.c. of nitrogen at 20° and 749 mm.
Found, N = 18·15; $C_{17}H_{20}O_2N_4$ requires N = 17·93 per cent.

There was still a large quantity of aldehyde in the portion of the oil which could not be distilled. It was got rid of by shaking with an aqueous solution of sodium hydroxide in the cold. The insoluble oil was extracted with ether and the solution dried with

calcium chloride.

It was a viscous brown oil of weight 5 gms. When heated with hydrobromic acid (constant boiling) to 100° in a sealed tube, it was completely decomposed, carbon separating out. This was filtered off and the filtrate evaporated to dryness. A small black residue remained which was not a hydroxy-acid.

ETHYL FORMYLETHOXYACETATE.

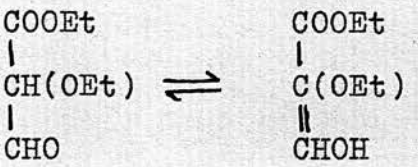
For the preparation of this, the method given for the analogous substance ethyl formylphenylacetate was followed.(1) 15·5 gms. of sodium wire was placed in a flask with 600 c.c. of ether (dried over sodium and phosphorus pentoxide). Into this a mixture of 90 gms. of ethyl ethoxyacetate and 60 gms. of ethyl formate (a slight excess) was poured. The mixture was warmed in order to start the reaction, which then proceeded somewhat vigorously, and required to be slowed by cooling in ice water. In the course of an hour or two the sodium dissolved leaving a yellow turbid liquid which, on standing, deposited a slimy substance. This was the sodium compound of ethyl formylethoxyacetate. The mixture was shaken out twice with water which dissolved the sodium compound,

(1) cf. Ann., 291, 164; and 391, 248.

the unused esters remaining in the ethereal layer. The aqueous layer was extracted with fresh ether. On acidification, an oil was liberated which was taken up in ether. After filtering through dry filter paper, the ether was distilled off, and the remaining oil taken over under reduced pressure. The ester distilled at 95-110° at 15 mm. Yield 63 gms.

The compound has an irritating odour when freshly distilled. It is rather viscous, and its solution in alcohol gives an intense blue-violet colouration with ferric chloride.

It may be assumed to exist in at least two tautomeric forms (like ethyl formylphenyl-acetate and ethyl formyl-propionate):-



The product obtained direct from the sodium compound became quite viscous in a few days. The molecular weight after standing for a week was 190. The normal value is 160. Alcohol and acetone gave similar results (Beckmann's boiling point method). After a month the figure had risen to 231 in alcohol and 270 in benzene; after four months the value was still 270. On combustion figures close to the calculated ones were obtained.

·1744 gm. gave ·3346 gm. of carbon dioxide and ·1192 gm. of water.

Found, C = 52·33, H = 7·66; $C_7H_{12}O_4$ requires C = 52·47, H = 7·56 per cent.

It was not found possible to narrow the boiling point range by fractional distillation. Each fraction when redistilled boiled over a wider range than before, and some decomposition took place towards the end of the distillation. Finally a series of fractions resulted having boiling points from 85 to 150° and upwards at 15 mm. Each gave the same reactions as the freshly prepared substance, but none gave analysis figures which were quite as close.

Michael states that ethyl formylpropionate, $OHC.CH(CH_3).COOEt$, is unstable at ordinary temperatures, and requires to be redistilled before use.(1)

No sodium bisulphite or copper compounds could be obtained.

The ester is very readily oxidised. Dilute neutral permanganate attacks it at once with formation of oxalic acid. (Pechmann (2) obtains benzoyl formic acid by oxidation of ethyl phenylformylacetate).

Action of ammonia on the ester. The ester was dissolved in dry ether and dry ammonia gas passed in, while the solution was cooled in ice. A white

(1) Ber., 38, 44 (footnote).
(2) Ber., 25, 1054.

flocculent precipitate was formed immediately (presumably the addition compound), but appeared to be unstable, passing into an oily substance which did not give the original aldehyde on treatment with acid.

Action of phenylhydrazine.. When treated with two molecular proportions of phenylhydrazine and warmed, a solid substance is obtained. This can readily be recrystallised from chloroform, and is a canary-yellow powder, crystalline when seen under the microscope. It is somewhat soluble in alcohol. It is the phenylhydrazide of formylethoxyacetic acid phenylhydrazone,

CO.NH.NH.Ph
|
CH(OEt)
|
CH.N:NH.Ph .

When heated suddenly, it melts at 228-229°.

·1212 gm. gave 19·30 c.c. of nitrogen at 13·5° and 725 mm.

·1629 gm. gave ·3983 gm. of carbon dioxide and ·0935 gm. of water.

Found C = 65·16, H = 6·43, N = 18·09;
$C_{17}H_{20}O_2N_4$ requires C = 65·33, H = 6·47, N = 17·93 per cent.

DE-ETHYLATION OF ETHYL DIETHOXYSUCCINATE.

Purdie & Barbour [1] obtained d-tartaric acid from d-dimethoxysuccinic acid by heating in a sealed tube with fuming hydrøiodic acid for eight hours at 100°.

An almost quantitative yield was obtained from ethyl diethoxysuccinate by using a saturated solution of hydrobromic acid. Four hours at 100° was found to be sufficient. The solution was then quite colourless, and there was a large layer of ethyl bromide. The acid was isolated by evaporation on the steam-bath, when it appeared as crystals.

Eight hours at 150° completely decomposed the substance: the mixture was black with carbon and a very great pressure was generated in the tube.

DIETHOXYSUCCINAMIDE.

The ester was treated with excess of concentrated ammonia and sufficient alcohol to keep it in solution. The mixture was allowed to stand in the cold for a few days, when white crystals made their appearance. The solution was evaporated to dryness over sulphuric acid, and the amide recrystallised.

(1) Jour. Chem. Soc., 79, 972.

It dissolves fairly readily in water, slightly in absolute alcohol, but is insoluble in ether. It can be recrystallised from rectified spirits. The crystals are small, light, and feathery. They melt, when quickly heated, at 241-242°, with decomposition.

·2338 gm. gave 25·43 c.c. of nitrogen at N.T.P. Found, N = 13·59; $C_8H_{16}O_4N_2$ requires N = 13·72 per cent.

POTASSIUM DIETHOXYSUCCINATE.

This was obtained by saponifying the ester with alcoholic potash. The salt crystallised out on cooling, and was filtered off. It was recrystallised from rectified spirits, when it appeared as long, slender needles, somewhat deliquescent. It is very soluble in water, slightly in absolute alcohol, and insoluble in acetone, which precipitates it from alcoholic solutions.

·2244 gm. of the thrice recrystallised salt gave ·1381 gm. of potassium sulphate on ignition with sulphuric acid.

Found, K = 27·62; $C_8H_{12}O_6K_2$ requires K = 27·66 per cent.

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d-DIETHOXYSUCCINIC ACID.

The ester was saponified by boiling with aqueous potassium hydroxide under a reflux. The mixture was acidified with hydrochloric acid and taken to dryness in a flask under reduced pressure. The residue was extracted with ether, the extract dried over calcium chloride, and the ether evaporated off. The acid was recrystallised from a mixture of three parts of benzene and one of ether, and a second time from ethyl acetate. Its m.p. was 126-128° (corr.) Purdie & Pitkeathly give 126-128°.

·08405 gm. of the acid required for neutralisation 16·38 c.c. of N/20 baryta. The calculated figure is 16·32 c.c.

Optical rotation of acid. In a 200 mm. tube an aqueous solution of the acid of concentration 2·1696 gms. per 100 c.c. gave a rotation of 2·887° at 20°.

Hence $[\alpha]_D^{20} = +66·53°$. (P.& P. give +66·51°).

Dissociation constant of acid. Following is a table of results:-

Temp. = 25°.

V	μ	100m	K
16	43·08	11·71	·097
32	59·70	16·23	·098
64	81·70	22·2	·099
128	110·1	29·9	·100
256	145·4	39·5	·101
512	188·2	51·2	·105
1024	238·0	64·7	·116
2048	292·0	79·4	·149

μ_∞ = 368. K = ·097.

Under the same conditions tartaric acid gave:-

V	μ	K
64	86·51	·109 (Ostwald ·102).
128	116·3	·110 (" ·103).

μ_∞ = 373.

The figures given as Ostwald's have been recalculated from his results [1] taking the ohm as unit of resistance in place of the Seimens' unit.

It will thus be seen that sym-d-diethoxy-succinic acid has a constant which is slightly less than that of tartaric acid.

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(1) Zeit. für Phys. Chem., 3, 371.

ELECTROLYSIS OF POTASSIUM ETHOXYACETATE.

A saturated solution containing 30 gms. of the salt was electrolysed, a current of 3 amperes being passed for two hours. An oily layer was seen to separate soon after the commencement of the electrolysis. This was taken up in ether, the solution dried, and the ether removed. 2·5 gms. of an oily product remained. The bulk of this distilled at 90° and gave formaldehyde on treatment with dilute acids. It was formaldehyde diethyl-acetal, $CH_2(OEt)_2$. There was a very small quantity of boiling point 130-200° which was not investigated.

The aqueous residue contained much formaldehyde and ethyl alcohol. The latter was separated by distilling over some of the liquid and saturating the distillate with potassium carbonate: the alcohol formed a separate layer.

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iso-AMYL iso-AMYLOXYACETATE.

Amyl chloracetate was added in small portions at a time to a solution of sodium amyloxide in amyl alcohol. A slight excess of amyloxide was employed. After standing overnight, the mixture was poured into water, neutralised with dilute hydrochloric acid, and the water separated off. The ester was freed from amyl alcohol and water by distillation. It came over at 240-250°, and after a few fractionations was obtained boiling at 248°. The yield was almost quantitative. Sp. gr. at 15/15° = ·911.

·2213 gm. gave ·5592 gm. of carbon dioxide and ·2262 gm. of water.

Found, C = 66·51, H = 11·06; $C_{12}H_{24}O_3$ requires C = 66·60, H = 11·19 per cent.

Action of sodium amyloxide on ethyl chloracetate. When ethyl chloracetate was added to a solution of sodium amyloxide in amyl alcohol, only a very small quantity of ethyl amyloxyacetate was obtained from the reaction mixture. The bulk of the product consisted of amyl amyloxyacetate.

Purdie has shown that one alkyl group is readily substituted for another in presence of sodium alkyloxide.(1)

(1) Jour. Chem. Soc., 51, 627. cf. also Walker & Appleyard, Jour. Chem. Soc., 67, 773.

SODIUM iso-AMYLOXYACETATE.

This was obtained by saponifying the ester with aqueous-alcoholic sodium hydroxide. It is very soluble in water and alcohol, but can easily be recrystallised from acetone. It appears as lustrous, soapy plates.

·2158 gm. when ignited with sulphuric acid gave ·0931 gm. of sodium sulphate.

Found, Na = 14·0; $C_7H_{13}O_3Na$ requires Na = 13·7 per cent.

ELECTROLYSIS OF SODIUM iso-AMYLOXYACETATE.

Owing to the tendency of this substance to froth when the ordinary platinum crucible apparatus is used, the electrolysis was carried out in a small beaker. A layer of mercury functioned as cathode, and a spiral of platinum wire wound round suitably shaped glass tubing was used as anode. A current of water was led through the tubing during electrolysis, and this, together with ice-water in which the beaker was immersed, provided very efficient cooling.

This apparatus was not merely convenient in that it allowed room for frothing; the tendency to froth was almost entirely eliminated. The liquid

became acid to litmus shortly after the commencement of the electrolysis, the sodium being retained by the mercury. It was found possible to pass a current of 3 to 4 amperes, whereas with the platinum crucible even ¼ amp. produced a very persistent froth of large volume.

40 c.c. of saturated solution (containing about 16 gms of solid) were electrolysed at a time, yielding 8 to 10 gms. of an oil. This was taken up in ether, and the solution dried with sodium sulphate. A total of 108 gms. of oil was collected in this way.

INVESTIGATION OF THE PRODUCTS OF ELECTROLYSIS.

The aqueous residue had a strong odour of formaldehyde.

The oil was distilled, and proved to be a very complex mixture. The main fractions were, however, identified. These were as follow:-

1. 87-100°. In spite of the fact that the ethereal solution was thoroughly dried, this fraction came over in two layers, one aqueous. They were separated, and the oily layer again dried in ethereal solution. On redistillation, however, an aqueous layer again appeared. The substance gave the reactions of an aldehyde, and the

liberation of water was thought to be the result of some condensation process. From the boiling point it was suspected to be iso-valeric aldehyde (b.p. 92°). The sodium bisulphite compound was readily prepared, and an estimation of the sodium content showed the substance to be that aldehyde.

·2209 gm. when ignited with sulphuric acid gave ·0840 gm. of sodium sulphate.

Found, Na = 12·3; $C_5H_{11}O_4NaS$ requires Na = 12·1 per cent.

2. 190-215°. It was expected that this fraction would contain the synthetic product if any had been formed. It was boiled with concentrated alcoholic potash to remove any esters present. The mixture was poured into water and extracted with ether. This treatment reduced the quantity only by a little, about 2 c.c. of a clear liquid being left. By repeated fractionation, a substance of boiling point 207-209° was isolated. It was not the diamyl ether of tetramethylene glycol. When hydrolysed with hydrochloric acid, amyl alcohol was obtained. This suggested that it might be formaldehyde diamylacetal, $CH_2(OC_5H_{11})_2$, whose b.p. is 207°. A density determination was made, and a value of ·837 found. The density of formaldehyde diamylacetal is ·835. An analysis

established the identity of the oil with this substance.

·1607 gm. gave ·4097 gm. of carbon dioxide and ·1850 gm of water; and ·1245 gm. gave ·3197 gm. of carbon dioxide and ·1421 gm. of water.

Found, C = 69·55, 69·61, H = 12·91, 12·80; $C_{11}H_{24}O_2$ requires C = 70·13, H = 12·86 per cent.

3. 240-250°. This fraction constituted about two thirds of the mixture. Alcoholic potash saponified it, giving amyl alcohol and an oily acid sparingly soluble in water. From its insoluble silver and copper salts, and its molecular weight by titration, this appeared to be amyloxyacetic acid. The amide was prepared from the original ester, and showed, after recrystallisation, a m.p. of 58°. The substance was therefore the amyl ester of amyloxyacetic acid, which has already been described.

In the mixture no amyl alcohol could be detected.

---

iso-AMYLOXYACETAMIDE.

The ester was treated with concentrated ammonia and alcohol, and allowed to stand for several days. The liquid was concentrated by evaporation

over sulphuric acid and extracted with ether. The amide was left as a white solid on removing the ether.

It is readily soluble in most of the organic solvents and in water. It can conveniently be crystallised from petroleum ether, which deposits it in small needles matted together. After three recrystallisations the m.p. was 58°.

·3235 gm. gave 26·4 c.c. of nitrogen at 15° and 758·2 mm.

Found, N = 9·65; $C_7H_{15}O_2N$ requires N = 9·65 per cent.

DISCUSSION OF RESULTS.

It will be seen that from none of the compounds electrolysed has any appreciable amount of synthetic product been obtained. In only one case was the quantity sufficiently great to admit of detection. This does not necessarily preclude the possibility that the desired doubling of radicals has taken place to a small extent in the other cases also: tartaric acid is an exceptionally easy compound to detect in traces.

The chief products of electrolysis are of an aldehydic nature. The replacement of a hydroxyl by an alkyloxy- group in the salt to be electrolysed has not prevented the formation of these compounds. This would suggest that their formation is not due to oxidation phenomena, since an ether group is not readily oxidised to an aldehyde group in this way:-

$$>CHOR \longrightarrow -CHO$$ (cf. page 6).

A further objection to any oxidation theory is provided by the formation of ethyl formylethoxy-acetate from potassium ethyl diethoxysuccinate. This substance is very readily oxidised, and it is hardly likely that it would appear as the result of a process of oxidation by so energetic a reagent as nascent oxygen at a platinum surface.

On the other hand Hofer & Moest's explanation

of the formation of formaldehyde from sodium glycollate (page 6) is applicable to alkyloxy- as well as to hydroxy-compounds, alcohol instead of water splitting off from the intermediate compound. The process is represented by the following equations:-

(1). $-CH\begin{matrix}OR\\COO\end{matrix} + OH \longrightarrow -CH\begin{matrix}OR\\OH\end{matrix} + CO_2.$

(2). $-CH\begin{matrix}OR\\OH\end{matrix} \longrightarrow -CH{=}O + R.OH$

That such an intermediate compound is indeed formed has been proved by the identification of the alcoholate of ethyl glyoxylate in the mixture resulting from the electrolysis of potassium ethyl ethoxymalonate. In this case the alcoholate is quite stable, showing no tendency to decompose into the alcohol and ethyl glyoxylate. (As vigorous a reagent as phosphorous pentoxide is required to remove the alcohol).

It is thought extremely probable that the mechanism of formation of this intermediate compound is that represented in equation (1) above. The other possible ways in which a hydroxy-compound could be formed, which have been outlined on pages 7 and 8, do not seem to furnish any adequate explanation of the observed facts.

Thus no proof of ester formation according to the equation:

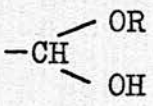
$$2RCOO \longrightarrow CO_2 + RCOOR$$

has been obtained. In any case only small quantities of ester have been found by previous workers.

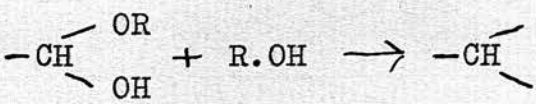
Bouveault's reaction must also be passed over: no compound of the nature RH has been found. As this would have been present in equal quantity with the hydroxy-compound, in accordance with Bouveault's equation, it could not have escaped observation.

In only one of the four cases investigated, that of potassium ethyl diethoxysuccinate, is it possible for an unsaturated body to be formed such as will give the required product by addition of the elements of water, and in this case no unsaturated compound was found.

Further evidence of the formation of the intermediate compound



is afforded by the presence of acetals in the mixtures resulting from the electrolysis of potassium ethoxy-acetate, sodium amyloxyacetate, and potassium ethyl ethoxymalonate. It is difficult to see how these could be produced other than by the action of the alcohol on the intermediate product in the neighbourhood of the anode.



As would be expected, oxidation products appear in every case, but only in relatively small quantities.

The behaviour of potassium ethoxyacetate has been shown to be quite analogous to that of the methoxyacetates.

The effect of replacing the ethoxy- by an amyloxy- group in acetic acid is very marked, the amount of electrolytic oil being increased by about four times. This increase is due to the presence of amyl amyloxyacetate. That the amyl alcohol liberated at the anode simultaneously with the formaldehyde is in a peculiarly active state, is shown by the formation of the acetal. It is clear, therefore, that if any amyloxyacetic acid were liberated at the anode, the necessary material for ester formation would be present, and it is almost certain that this is the source of the ester. The acid can be assumed to result from the well known reaction represented in the following equation:-

$$2CH_2(OC_5H_{11})COO + H_2O \longrightarrow 2CH_2(OC_5H_{11})COOH + (O).$$

When salts of aromatic acids are electrolysed, the free acid is almost invariably regenerated in quantity, and it would appear as though the presence of the amyloxy- group has caused the sodium amyloxy-acetate to behave in a similar manner.

SUMMARY.

1. Four compounds have been electrolysed and the nature of the resulting products investigated. These are:-

(a) Potassium ethyl ethoxymalonate, which gave ethyl diethoxyacetate, the alcoholate of ethyl glyoxylate, a little ethyl diethoxysuccinate, ethyl alcohol, oxalic acid, formaldehyde, and acetaldehyde.

(b) Potassium ethyl diethoxysuccinate, which gave ethyl formylethoxyacetate, oxalic acid, ethyl oxalate, ethyl alcohol, formaldehyde, and formic acid.

(c) Potassium ethoxyacetate, which gave formaldehyde, alcohol, and formaldehyde diethylacetal.

(d) Sodium amyloxyacetate, which gave amyl amyloxyacetate, formaldehyde diamylacetal, formaldehyde, and iso-valeric aldehyde.

2. In the course of the investigation the following new compounds have been prepared and their properties described:- Ethoxymalonamide, ethyl formylethoxyacetate, the phenylhydrazide of formylethoxyacetic acid phenylhydrazone, d-diethoxysuccinamide, potassium diethoxysuccinate, iso-amyl iso-amyloxyacetate, and iso-amyloxyacetamide.

3. The dissociation constants of ethoxymalonic and d-diethoxysuccinic acids have been determined, and that of tartronic acid verified.
